

Interfacial Polymerization of Polyaniline Nanofibers Grafted to Au Surfaces

10 August 2004

Prepared by

D. D. SAWALL, R. M. VILLAHERMOSA,
R. A. LIPELES, and A. R. HOPKINS
Space Materials Laboratory
Laboratory Operations

Prepared for

SPACE AND MISSILE SYSTEMS CENTER
AIR FORCE SPACE COMMAND
2430 E. El Segundo Boulevard
Los Angeles Air Force Base, CA 90245

Engineering and Technology Group

This report was submitted by The Aerospace Corporation, El Segundo, CA 90245-4691, under Contract No. FA8802-04-C-0001 with the Space and Missile Systems Center, 2430 E. El Segundo Blvd., Los Angeles Air Force Base, CA 90245. It was reviewed and approved for The Aerospace Corporation by P. D. Fleischauer, Principal Director, Space Materials Laboratory. Michael Zambrana was the project officer for the Mission-Oriented Investigation and Experimentation (MOIE) program.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

A handwritten signature in dark ink, appearing to read "Michael Zambrana", is written over a horizontal line.

Michael Zambrana
SMC/AXE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) 10-08-2004		2. REPORT TYPE		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Interfacial Polymerization of Polyaniline Nanofibers Grafted to Au Surfaces				5a. CONTRACT NUMBER FA8802-04-C-0001	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) D. D. Sawall, R. M. Villahermosa, R. A. Lipeles, and A. R. Hopkins				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The Aerospace Corporation Laboratory Operations El Segundo, CA 90245-4691				8. PERFORMING ORGANIZATION REPORT NUMBER TR-2004(8565)-8	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Space and Missile Systems Center Air Force Space Command 2450 E. El Segundo Blvd. Los Angeles Air Force Base, CA 90245				10. SPONSOR/MONITOR'S ACRONYM(S) SMC	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) SMC-TR-04-20	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT In this work, polyaniline/poly(sulfonated styrene) nanofiber composites were prepared by an interfacial method. The <i>in-situ</i> polymerization technique of these PANI nanofibers in the presence of sulfonated polystyrene allowed for the growth of PANI 2-D nanostructures embedded in the polymerized sulfonated host. This facile approach enables a self-assembly of these nanofibers into a workable, robust, conductive composite that can be processed and cast from water. A low accelerating voltage SEM was used to image these twisted fibers within the bulk of the cast film. In addition, the SEM confirmed the self-assembly of these 40-50 nm fibers within the host PSS to yield an electrically conducting composite film.					
15. SUBJECT TERMS Nanofibers, Conductive polymers, Interfacial polymerization, Self-assembled					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES 5	19a. NAME OF RESPONSIBLE PERSON Alan Hopkins
a. REPORT UNCLASSIFIED	b. ABSTRACT UNCLASSIFIED	c. THIS PAGE UNCLASSIFIED			19b. TELEPHONE NUMBER (include area code) (310)336-5664

Acknowledgments

We would like to thank Dr. Nathan Presser (The Aerospace Corporation) for help with the SEM images, Dr. Hyun I. Kim for assistance with XPS, Dr. Bruce H. Weiller for helpful discussion, the NSF for funding through an IGERT fellowship (D.S), and The Aerospace Corporation IR&D program..

Figures

1. Schematic of the interfacial synthesis of polyaniline (PANI) nanofibers grafted onto a Au substrate using a self-assembled monolayer of 4-aminothiophenol (4-ATP) 2
2. Series of chips showing progression of nanofiber growth on surface 2
3. An SEM image of the chip from Figure 2 after a reaction time of 24 h shows a dense mat of nanofibers, completely obscuring the underlying gold interdigitated electrode 3

Organic nanowires, particularly those made from polyaniline (PANI), have recently received considerable attention due to their unique chemical sensing and electrical properties. Interest has been directed towards fine-tuning the synthesis of tubular morphologies by controlling reaction conditions. The method frequently employed to construct such morphologies has typically involved template-free chemical synthesis, in which the aniline monomer polymerizes in the presence of large bulky acids. For instance, Huang et al.¹ recently developed a simple, practical method using a bi-phasic or "interfacial" polymerization for making uniform, template-free² nanofibers. Furthermore, Wan et al.^{3,4,5,6} and others^{7,8} have developed a template-free solution method in which the diameter of the tube could be controlled by the dopant functionality and amount. Besides the many challenges in polymerizing these chains into nanosized tubes, the next largest hurdle is arranging these nanosized fibers onto a substrate in an ordered fashion for the purpose of fabricating useful, nanoscale devices such as chemiresistive vapor sensors. The ability to polymerize nanostructures directly on metallic substrates has been previously achieved by MacDiarmid,⁹ Hayes et al.,¹⁰ and Porter et al.¹¹ where electrochemical and Langmuir-Blodgett methods were used to grow and organize nanometer-sized polyaniline tubes on modified Au electrodes. Current methods for synthesizing covalently bound nanostructured PANI to metal surfaces require templates and utilize electrochemical or time-consuming lithography methods that produce low yields.

In this report we describe a simple, two-step process for the direct synthesis of conductive nanosized PANI fibers bound directly to the surface of a Au substrate. The process uses an interfacial polymerization technique to form a two-dimensional mesh of PANI fibers that were grafted to the Au surface using a self-assembled monolayer of 4-aminothiophenol (4-ATP). The two-step process is as follows: (1) A self-assembled monolayer (SAM) of 4-ATP is created on a Au surface, (2) then PANI nanofibers are directly synthesized onto the Au surface by placing the substrate at the interface of a biphasic solution of dopant and aniline monomer. The use of exact molar ratios of reactants facilitates the formation of the nanofibers.

The objective of the SAM formation step is to functionalize the Au surface with an amine that will promote covalent attachment of PANI. A SAM of 4-ATP was created using a standard monolayer formation technique,¹² and was confirmed by X-ray photoelectron Spectroscopy (XPS) and grazing angle IR-absorption measurements. During the polymerization, the 4-ATP-treated substrate sits at the interface of the organic/aqueous biphasic system (Figure 1) used to synthesize PANI nanofibers.¹ Using a high mole ratio of 1R-(-)-10-camphorsulfonic acid (dopant) to aniline monomer,¹ the polymerization is autocatalyzed by the presence of the doping acid and proceeds at a rapid rate. During the reaction, aniline monomer diffuses from the organic layer (bottom) to the interface, gets protonated by the acidic aqueous layer to form an anilinium cation (stabilized by the phenyl group), and then connects to the "tail" end of an oligomer. Nanofibers form in or near the interface, which suggests that species or conditions at the interface influence polymer morphology. In this template-free synthesis, the driving force(s) involved in forming nanofibers is unclear, but it is hypothesized that there may be preferential electrostatic interaction¹³ between the aniline monomer and the growing PANI chains that favor nanosized fiber formation.

The growth of these nanofibers on Au was monitored with a scanning electron microscope (SEM)¹⁴ by recording micrographs of chips that were submerged in the interfacial reaction mixture for 1, 3, and 5 min (Figures 2-b, c, d) and after 24 h (Figure 3). As shown in Figure 2-b, the growth of the polyaniline nanofibers begins with the formation of sub-micron finger-like projections emanating on

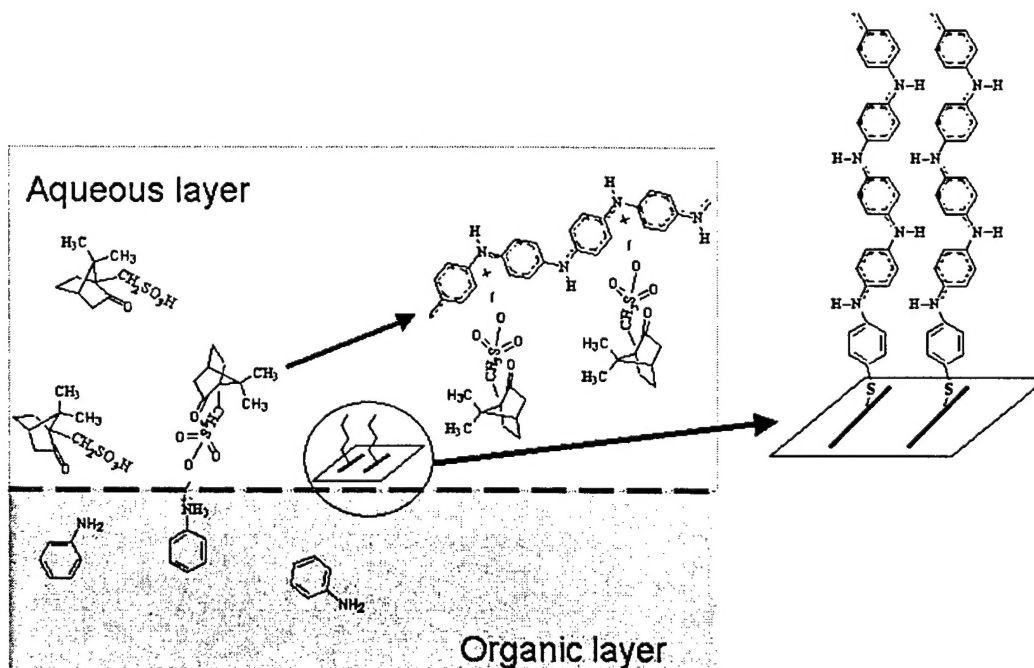


Figure 1. Schematic of the interfacial synthesis of polyaniline (PANI) nanofibers grafted onto a Au substrate using a self-assembled monolayer of 4-aminothiophenol (4-ATP). It is not clear whether the PANI grows directly off of the 4-ATP-modified gold surface or whether PANI is synthesized in solution at the interface and then diffuses to the gold surface where it "links" with the self-assembled monolayer of gold.

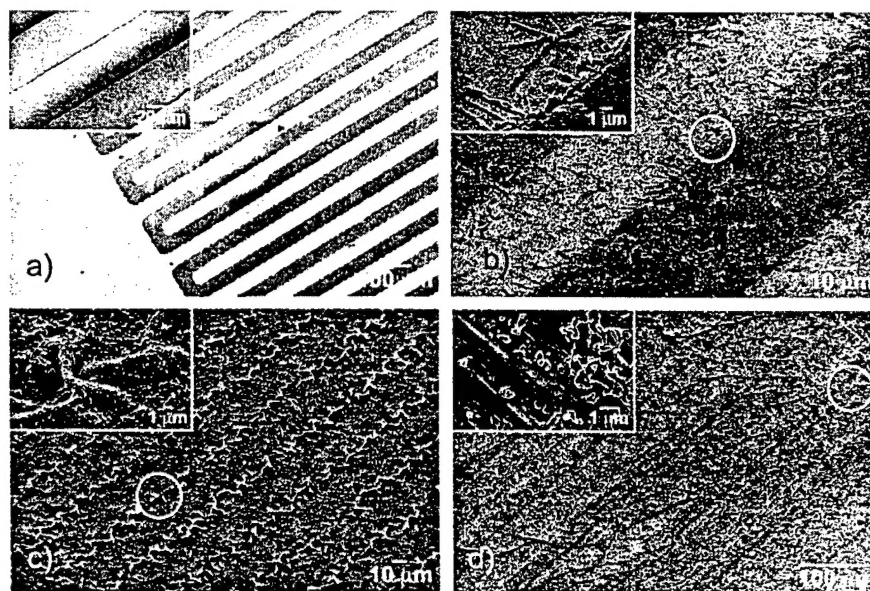


Figure 2. Series of chips showing progression of nanofiber growth on surface. (a) SEM image of a bare, interdigitated gold electrode pre-treated with a self-assembled monolayer of 4-aminothiophenol (light area). (b-c) SEM images following the growth of sub-micron sized PANI on a 4-aminothiophenol treated gold electrodes using an interfacial polymerization technique. The chips were removed from the reaction mixture and imaged after (b) 1 min, (c) 3 min, and (d) 5 min. Insets show magnification of the circled areas.

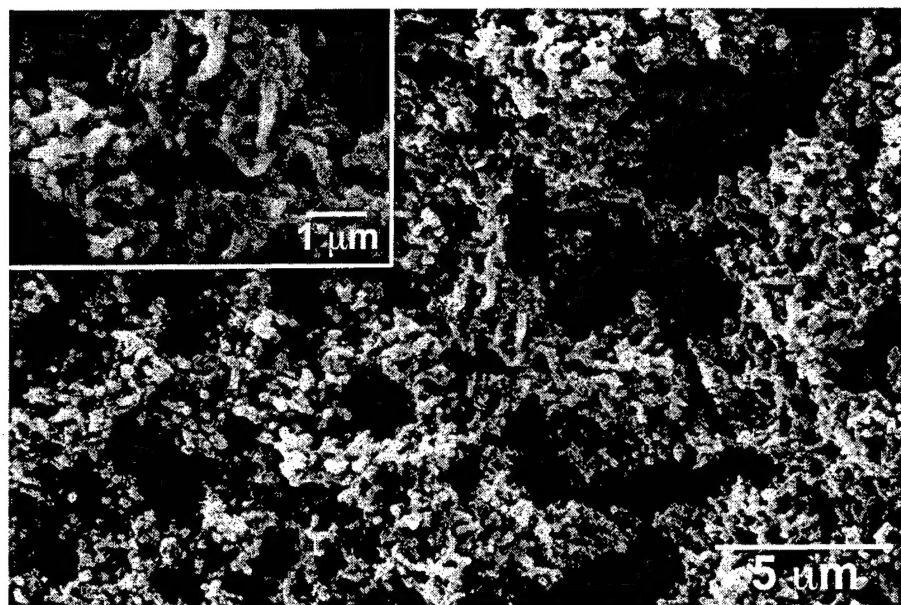


Figure 3. An SEM image of the chip from Figure 2 after a reaction time of 24 h shows a dense mat of nanofibers, completely obscuring the underlying gold interdigitated electrode.

the patterned Au surface. After 3 min, the Au surface is covered with two-dimensional interconnecting ribbon structures that span the Au strips. The growth of these sub-micron PANI structures, as seen in Figure 2-c, appears to be guided by the preabsorbed monolayer of 4-ATP. With increased polymerization time, these ribbon-like structures form rods (Figure 2-d) that are surrounded by amorphous aggregates. The rods serve as a new polymerization initiation site from which aniline nucleates and grows into nanosized fibers. After 24 h, both the Au and glass are covered by a thick mat of nanofibers (Figure 3), and to the eye has the appearance of a uniform green film. The fibers within this dense mat had nearly uniform diameters of 40–50 nm, which is consistent with interfacially grown fibers first observed by Huang et al.¹ The low resistance of the PANI nanofibers in Figure 4 across the interdigitated electrodes suggests a minimal amount of contact resistance at the interface between the PANI fibers and the Au.

To ensure that the PANI nanofibers are not merely physisorbed, the 4-ATP monolayer was substituted with a benzenethiol (BT). Using the same polymerization conditions that yielded the PANI nanofiber morphology in Figure 2, the same morphology was not observed with the BT-treated chip. This supports the notion that the 4-ATP directs the growth of the PANI on the surface of the substrate.

Although it has been clearly established in the literature¹⁵ and in our lab that PANI films grow on untreated substrates, the resulting adhesion is non-covalent and mechanically weak. The most important aspect of this novel procedure is the remarkable durability of the covalently bonded nanofibers to the Au interface. For instance, samples prepared without a 4-ATP SAM do not exhibit the same improved adhesion, nor do samples of neat PANI nanofibers drop cast onto a Au substrate preadsorbed with a monolayer of 4-ATP. Repeated finger abrasion and Scotch tape tests indicated improved adhesion of the covalently bonded PANI fibers compared to physisorbed samples. In addi-

tion to these simple abrasion tests, a series of acid/base exposures (doping/dedoping) showed little influence on the durability or conductivity of the PANI nanofibers. These two important physical and chemical durability experiments distinguish this method from other nanopatterning techniques for polyaniline on Au surfaces.

This is a preliminary report of a novel and easy method to chemically synthesize template-free polyaniline nanofibers directly onto a functionalized Au substrate. The 4-ATP SAM acts like an initial template, directing the growth of the PANI nanofibers into structured morphologies. The mechanism for this process is not well understood, but the covalent attachment of the PANI nanofibers to the Au leads to improved durability over current nanofiber fabrication techniques.

References and Notes

1. Huang, J., Virgi, S., Weiller, B. H., and Kaner, R.B., *J. Am. Chem Soc.*, **125**(2), 314, 2003.
2. Martin, C. R., Parthasarathy, R., and Menon, V., *Synth Metals*, **55**(2-3), 1165, 1993.
3. Wei, Z., Zhang, Z., and Wan, M. *Langmuir*, **18**, 917, 2002.
4. Liu, J. and Wan, M., *J. Mater. Chem.*, **11**(2), 404, 2001, (b) Cao, H.; Tie, C.; Xu, Z.
5. Yang, Y. and Wan, M., *J. Mater. Chem.*, **12**(4), 897, 2002.
6. Qiu, H.-J. and Wan, M., *Chinese J. Poly. Sci.*, **19**(1), 65, 2001.
7. Cao, H., Tie, C., Xu, Z., Hong, J. and Sang, H., *Appl. Phys. Lett.*, **78**(11), 1592, 2001.
8. Delvaux, M., Duchet, J., Stavaux, P.-Y., Legras, R., and Demoustier C., *Synth. Met.*, **113**(3), 275, 2000.
9. Juang, W.-S., Humphrey, B. D., MacDiarmid, A. G., *J. Chem. Soc., Faraday Trans. 1*, **82**, 2385, 1986.
10. Hayes, W. A. and Shannon, C., *Langmuir*, **14**, 1099, 1998.
11. Porter, L. A., Jr., Ribbe, A. E. and Buriak, J. M., *Nano Letters*, **3**(8), 1043, 2003.
12. Hayes, W. A. and Shannon, C., *Langmuir*, **12**, 3688, 1996.
13. Liu, W., Cholli, A. L., and Nagaragan, R., *J. Am. Chem. Soc.*, **121**, 11345, 1999.
14. To prevent charging, a low accelerating voltage of 2 kV was used to image the structures. At such a low accelerating voltage, it was not necessary to coat PANI with a conducting layer. A tip current of less than 6×10^{-12} A allowed images up to 30,000x magnification at 2 kV without charging.
15. Malinauskas, A., *Polymer*, **42**, 3957, 2001.

LABORATORY OPERATIONS

The Aerospace Corporation functions as an "architect-engineer" for national security programs, specializing in advanced military space systems. The Corporation's Laboratory Operations supports the effective and timely development and operation of national security systems through scientific research and the application of advanced technology. Vital to the success of the Corporation is the technical staff's wide-ranging expertise and its ability to stay abreast of new technological developments and program support issues associated with rapidly evolving space systems. Contributing capabilities are provided by these individual organizations:

Electronics and Photonics Laboratory: Microelectronics, VLSI reliability, failure analysis, solid-state device physics, compound semiconductors, radiation effects, infrared and CCD detector devices, data storage and display technologies; lasers and electro-optics, solid-state laser design, micro-optics, optical communications, and fiber-optic sensors; atomic frequency standards, applied laser spectroscopy, laser chemistry, atmospheric propagation and beam control, LIDAR/LADAR remote sensing; solar cell and array testing and evaluation, battery electrochemistry, battery testing and evaluation.

Space Materials Laboratory: Evaluation and characterizations of new materials and processing techniques: metals, alloys, ceramics, polymers, thin films, and composites; development of advanced deposition processes; nondestructive evaluation, component failure analysis and reliability; structural mechanics, fracture mechanics, and stress corrosion; analysis and evaluation of materials at cryogenic and elevated temperatures; launch vehicle fluid mechanics, heat transfer and flight dynamics; aerothermodynamics; chemical and electric propulsion; environmental chemistry; combustion processes; space environment effects on materials, hardening and vulnerability assessment; contamination, thermal and structural control; lubrication and surface phenomena. Microelectromechanical systems (MEMS) for space applications; laser micromachining; laser-surface physical and chemical interactions; micropropulsion; micro- and nanosatellite mission analysis; intelligent microinstruments for monitoring space and launch system environments.

Space Science Applications Laboratory: Magnetospheric, auroral and cosmic-ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; infrared surveillance, imaging and remote sensing; multispectral and hyperspectral sensor development; data analysis and algorithm development; applications of multispectral and hyperspectral imagery to defense, civil space, commercial, and environmental missions; effects of solar activity, magnetic storms and nuclear explosions on the Earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation, design, fabrication and test; environmental chemistry, trace detection; atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions, and radiative signatures of missile plumes.